Claims

1. Peptides that are able to form a complex with calcium, that contain phosphonate- or phosphate groups, and that are capable to protect teeth against acid attack, chosen from the group consisting of:
-bisphosphonylated-epsilon-polylysine (Bispho x elys),
-casein phosphopeptide epsilon-polylysine copolymer $(CPP\ x\ elys)_n$,
-hydrolyzed phosvitin that has been conjugated to epsilon polylysine $(Phos\text{-}h\ x\ elys)_n$,
-casein phosphopeptide that has been polymerized with a carbodiimide $(CPP)_n$ and
-phosvitin that has been hydrolyzed with trypsin, pepsin or a combination of both (Phos-h).

2.Chitosan hydrolysate, with a molecular weight of maximum 30kD, that has been conjugated with casein phosphopeptide (CPP) into $(CPP\ x\ hy\text{-}chit)_n$.

3. The use of amino-proteins that contain one or more components able to complex calcium ions, phospho-proteins that contain one or more components able to complex calcium ions, hydrolyzed chitosan that contains one or components able to complex calcium ions and/or amino-proteins or a mixture of such products to protect teeth against acid attack and/or to control the bacterial flora in the oral cavity,
wherein:

a) the amino-proteins that contain one or more components able to complex calcium ions are choosen from the group consisting of, bisphosphonylated epsilon-polylysine (Bispho x elys), biscarboxylated epsilon-polylysine, 3-hydroxy-phthalated epsilon-polylysine, proteins that are bisphosphonylated or biscarboxylated, and that have a molecular weight of at least 2kD and contain at least 40% of the amino acid lysine,

b) the phospho-proteins that contain one or more components able to complex calcium, are chosen from the group consisting of, polymerized casein phosphopeptide $(CPP)_n$, partially hydrolyzed phosvitin (Phos-h), casein phosphopeptide-epsilon-polylysine-copolymer $(CPP\ x\ elys)_n$, and copolymers of hydrolyzed phosvitin (Phos-h) or phosvitin (Phos) with epsilon-polysine or with hydrolyzed chitosan to respectively $(Phos\text{-}h\ x\ elys)_n$, $(Phos\text{-}h\ x\ hy\text{-}chit)_n$, $(Phos\ x\ elys)_n$ and $(Phos\ x\ hy\text{-}chit)_n$,

c) the hydrolyzed chitosan that contains one or more components able to complex calcium is, bisphosphonylated-hydrolyzed chitosan (Bispho x hy-chit) or casein phosphopeptide-hydrolyzed-chitosan-copolymer $(CPP\ x\ hy\text{-}chit)_n$, and

d) the amino-proteins are, epsilon-polylysine (elys) or polylysine.

4. The use according to claim 3. wherein said proteins are peptides.

5. The use of epsilon-polylysine or of polylysine according to claim 3. for the protection of teeth, for the control of the bacterial flora in the oral cavity or to treat halitosis.

6. The use of a phosvitin hydrolysate according to claim 3. wherein said phosvitin hydrolysate is obtainable by treating phosvitin with one or more proteases.

7. The use according to claim 6 wherein said phosvitin hydrolysate is obtainable by hydrolysing phosvitin with trypsin, chymotrypsin, pepsin, or a combination of said enzymes.

8. The use according to claim 3 wherein said bisphosphonylated epsilon-polylysine is 2-e-polylysine-1-hydroxyethane-1,1-diphosphonate , whereby the number of bisphosphonyl groups varies between one and the amount of amino groups that is present in the peptide.

9. The use according to claim 3 wherein said hydrolyzed chitosan has a molecular weight that is lower or equal to 30kD, and is obtainable by hydrolyzing chitosan by an acid or an enzyme.

10. A method to produce polymerized casein phosphopeptide $(CPP)_n$ in water characterized in that: casein phosphopeptide is polymerized with a water-soluble carbodiimide.

11. The method according to claim 10 wherein said carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide.

12. A method to produce casein phosphopeptide x epsilon-polylysine-copolymer $(CPP \times elys)_n$ in water characterized in that: casein phosphopeptide and epsilon-polylysine are conjugated with a water soluble carbodiimide.

13. The method according to claim 12 wherein said carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide.

14. The method to produce casein phosphopeptide x hydrolyzed-chitosan-copolymer $(CPP \times hy\text{-}chit)_n$ in water characterized in that: casein phosphopeptide

and hydrolyzed chitosan (with a molecular weight below or equal than 30kD) are conjugated with a water soluble carbodiimide.

15. The method according to claim 14 wherein said carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide.

16. The method to produce a copolymer from hydrolyzed phosvitin and epsilon-polylysine (Phos-h x elys)$_n$ characterized in that: phosvitin has been hydrolyzed with pepsin, trypsin, chymotrypsin (or a combination of such enzymes), and has been conjugated to epsilon-polylysine with a water-soluble carbodiimide such as 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide and/or with glutaminase.

17. The method to produce bisphosphonylated epsilon-polylysine from a mixture of hydrogen peroxide, epsilon-polylysine and vinylidene diphosphonate (in salt or acid form).

18. The method to produce bisphosphonylated epsilon-polylysine characterized in that: epsilon-polylysine is allowed to react with a bisphosphonylated epoxide at a pH from 3 to 9.

19. The method according to claim 18 wherein some of the substituents on the epoxide consists of hydrogen or alkyl groups and wherein the phosphonyl groups are esterified or exist in the acid (H^+) or salt (Na^+, K^+, other) form or a mixture.

20. The method according to claim 18 wherein the bisphosphonylated epoxide is epoxyethane-1,1-diphosphonate.

21. The method according to claim 18 wherein the reaction is carried out at a pH of between 3 to 6 and with a BF_3 catalyst.

22. The method according to claim 18 wherein the reaction is carried out in water or in a mixture of water and alcohol.

23. The method according to claim 22 wherein the term alcohol refers to methanol, ethanol, isopropanol or butanol.

24. The method to produce bisphosphonylated epsilon-polylysine characterized in that: epsilon polylysine, that has been denaturated with a denaturating agent such as urea, is allowed to react with a bisposphonylated epoxide at a pH of between 3 to 9.

25. The method to produce 3-hydroxy-phthalated epsilon-polylysine from epsilon-polylysine and 3-hydroxyphthalic anhydride.

26. The use of the compounds indicated in claims 1 to 9 as ingredient or combination of ingredients, in products for oral care such as toothpaste, mouth-refreshing solution, mouth sprays and gels, chewing gum,
candies and other food systems, artificial saliva's, medical oral care products for the treatment of teeth from patients with xerostomia, oral cancer, Hodgkin's disease, Sjögren syndrome, HIV, diabetes.

27.The use of the compounds indicated in claims 1 to 9, according to claim 26, in combination with additional ingredients such as fluoride, anticariogenic sugars, peptides for remineralisation, antibacterial products, vaccins, anti-bodies, acid absorbing ingredients, encapsulated ingredients,
thickeners, anionic, nonionic, cationic or amphoteric detergents, humidifiers, abrasive ingredients, anti-tooth stone, aroma's, preservatives, cooling agents, anti-sensitive ingredients and/or sweeteners.